

# Synthesis and Characterization of a Novel Coordination Complex Based on Fluorescein

ZHANG Guan-Hua<sup>(1, 2)</sup>(张冠华); WU Xiao-Yuan<sup>(1)</sup>(吴小园); WANG Sa-Sa<sup>(1)</sup>(王洒洒); JIANG Xiao-Yu<sup>(3)</sup>(蒋晓瑜); LU Can-Zhong<sup>(1)</sup>(卢灿忠)

<sup>(1)</sup> Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China; <sup>(2)</sup> Graduate University of Chinese Academy of Sciences, Beijing 100049, China; <sup>(3)</sup> Fujian University of Technology, Fuzhou 350108, China

**ABSTRACT** A novel coordination complex,  $\{[\text{Cd}_2(\text{C}_{20}\text{H}_{10}\text{O}_5)_2(\text{H}_2\text{O})_4] \cdot 10\text{H}_2\text{O}\}_n$ , has been synthesized based on fluorescein (2-(6-hydroxy-3-oxo-3H-xanthen-9-yl) benzoic acid) and systematically characterized by elemental analysis, infrared (IR) spectrum, thermo gravimetric analysis (TGA), powder X-ray diffraction (PXRD) and single-crystal X-ray diffraction. Compound **1** crystallizes in monoclinic, space group  $P2_1/n$  with  $a = 20.428(5)$ ,  $b = 8.084(2)$ ,  $c = 21.689(5)$  Å,  $\beta = 96.360(5)^\circ$ ,  $M_r = 993.46$ ,  $V = 3559.7(15)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.845$  g/cm<sup>3</sup>,  $\mu = 1.276$  mm<sup>-1</sup>,  $F(000) = 1974.0$ ,  $GOOF = 1.044$ ,  $\lambda(\text{MoK}\alpha) = 0.71073$  Å, the final  $R = 0.0553$  and  $wR = 0.1720$  for 7245 observed reflections with  $I > 2\sigma(I)$ .

**Keywords:** crystal structure; coordination complex; fluorescein;

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## 1 INTRODUCTION

The design and synthesis of coordination complexes have been one of the most attracting points in coordination polymers<sup>[1-5]</sup> as a result of their structural diversity and versatile applications in various areas including photochemistry<sup>[6]</sup>, catalysis<sup>[7]</sup>, gas-absorption and separation<sup>[8, 9]</sup>, energy storage and conversion<sup>[10, 11]</sup>, etc. Employing functional ligands has become a widespread method to purposively construct coordination polymers with certain structures and properties<sup>[12-15]</sup>. Fluorescein, a classic dye which was synthesized in the 19th century firstly<sup>[16]</sup>, has particularly arisen our interest recently since it is widely used in human's daily life as colorant and biochemical probes due to its broad emitting spectrum, high fluorescence quantum yield and non-toxic property<sup>[17, 18]</sup>. Among all the reported metal coordination complexes with fluorescein, few of them are companied with crystal structures<sup>[19, 20]</sup>.

Herein we report the synthesis and structure of a six-coordinated cadmium complex based on fluorescein,  $\{[\text{Cd}_2(\text{C}_{20}\text{H}_{10}\text{O}_5)_2(\text{H}_2\text{O})_4] \cdot 10\text{H}_2\text{O}\}_n$  (**1**), which possesses a unique  $\text{Cd}_2\text{O}_{10}$  cluster.

## 2 EXPERIMENTAL

### 2.1 Materials and instruments

All the solvents and reagents were purchased from commercial sources of AR grade and used without further purification. Infrared (IR) spectrum was measured on a Vertex 70 using KBr pallet. Elemental analysis tests of **1** were carried out employing a Vario EL-Cube elemental analyzer. Thermo gravimetric analysis (TGA) was performed employing a TGA/DSC 1 STAR<sup>e</sup> system at a heating rate of 10 °C/min under nitrogen atmosphere. Powder X-ray diffraction (PXRD) was performed at room temperature on a Rigaku MiniFlex II diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154$  nm).

### 2.2 Synthesis procedures

Fluorescein (16.7 mg, 0.05 mmol) was dissolved in 1.8 mL DMF, then 2.2 mL aqueous solution of  $\text{Cd}(\text{NO}_3)_2$  (14.9 mg, 0.05 mmol) was added. After ten minutes supersonic processing in open air, the mixture was sealed in a 10 mL glass vessel, which was heated to 383 K and kept for two days, and then slowly cooled to room temperature for another two days. Red block single crystals were filtrated and washed with pure water, and dried in air. Yield 27% (based on fluorescein). Calculated (%): C, 49.71; H, 2.90; O, 23.18. Found (%): C, 49.16; H, 2.72; O, 23.85.

### 2.3 X-ray crystallographic study

A suitable red prism single crystal of **1** was selected and mounted on a glass fiber for single-crystal X-ray diffraction. The SCXRD test was performed on a Saturn 724+ CCD diffractometer with  $\text{MoK}\alpha$  irradiation ( $\lambda = 0.71073$  Å) at  $T = 293$  K. Data reduction was processed using CrystalClear software and the cell parameters were reduced and refined by the same one. The structures were solved and refined by Olex2-1.2.8 using ShelXS program *via* Direct Method to solve and ShelXL by least-squares method to refine. All non-hydrogen atoms were refined anisotropically. One of the O atoms of the carboxyl on fluorescein is disordered and modeled on two sites. The hydrogen atoms for fluorescein ligands were placed in calculated positions and treated as riding on their parents before the final cycle of refinement, while the hydrogen atoms of unbound water molecules were not presented because the great vibration makes it hard to fix. A total of 8161 reflections

of **1** were collected in the range of  $2.52 \leq \theta \leq 27.49^\circ$  using an  $\omega$ -scan mode ( $-26 \leq h \leq 25$ ,  $-10 \leq k \leq 10$ ,  $-28 \leq l \leq 28$ ), of which 7245 were independent with  $R_{\text{int}} = 0.0377$ . The final  $R = 0.0552$  and  $wR = 0.1716$  for 8161 observed reflections with  $I > 2\sigma(I)$ .  $(\Delta/\sigma)_{\text{max}} = 0.001$ . The selected bond lengths and bond angles related to Cd1 and Cd2 for **1** are listed in Table 1.

**Table 1. Selected Bond Lengths (Å) and Bond Angles ( $^\circ$ )**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)–O(1) <sup>a</sup>	2.218(4)	Cd(1)–O(11)	2.361(5)	Cd(2) <sup>c</sup> –O(8) <sup>d</sup>	2.250(4)
Cd(1)–O(3) <sup>b</sup>	2.249(3)	Cd(1)–O(12)	2.307(4)	Cd(2) <sup>c</sup> –O(10)	2.268(3)
Cd(1)–O(5)	2.271(3)	Cd(2) <sup>c</sup> –O(5)	2.275(3)	Cd(2) <sup>c</sup> –O(13) <sup>c</sup>	2.321(4)
Cd(1)–O(10)	2.267(3)	Cd(2) <sup>c</sup> –O(6) <sup>c</sup>	2.238(4)	Cd(2) <sup>c</sup> –O(14) <sup>c</sup>	2.362(5)
Angle	( $^\circ$ )	Angle	( $^\circ$ )	Angle	( $^\circ$ )
Cd(1)–O(5)–Cd(2) <sup>c</sup>	104.1(1)	O(5)–Cd(1)–O(10)	75.8(1)	O(6) <sup>c</sup> –Cd(2) <sup>c</sup> –O(8) <sup>d</sup>	93.6(1)
Cd(1)–O(10)–Cd(2) <sup>c</sup>	104.2(1)	O(5)–Cd(1)–O(11)	91.4(2)	O(6) <sup>c</sup> –Cd(2) <sup>c</sup> –O(10)	96.8(1)
O(1) <sup>a</sup> –Cd(1)–O(3) <sup>b</sup>	95.2(1)	O(5)–Cd(1)–O(12)	169.8(1)	O(6) <sup>c</sup> –Cd(2) <sup>c</sup> –O(13) <sup>c</sup>	93.1(1)
O(1) <sup>a</sup> –Cd(1)–O(5)	99.0(1)	O(10)–Cd(1)–O(11)	82.6(2)	O(6) <sup>c</sup> –Cd(2) <sup>c</sup> –O(14) <sup>c</sup>	91.7(2)
O(1) <sup>a</sup> –Cd(1)–O(10)	172.2(1)	O(10)–Cd(1)–O(12)	94.2(1)	O(8) <sup>d</sup> –Cd(2) <sup>c</sup> –O(10)	97.7(1)
O(1) <sup>a</sup> –Cd(1)–O(11)	91.9(2)	O(11)–Cd(1)–O(12)	85.2(2)	O(8) <sup>d</sup> –Cd(2) <sup>c</sup> –O(13) <sup>c</sup>	86.6(1)
O(1) <sup>a</sup> –Cd(1)–O(12)	90.8(1)	O(5)–Cd(2) <sup>c</sup> –O(6) <sup>c</sup>	171.9(1)	O(8) <sup>d</sup> –Cd(2) <sup>c</sup> –O(14) <sup>c</sup>	168.8(2)
O(3) <sup>b</sup> –Cd(1)–O(5)	96.9(1)	O(5)–Cd(2) <sup>c</sup> –O(8) <sup>d</sup>	90.5(1)	O(10)–Cd(2) <sup>c</sup> –O(13) <sup>c</sup>	168.9(1)
O(3) <sup>b</sup> –Cd(1)–O(10)	91.1(1)	O(5)–Cd(2) <sup>c</sup> –O(10)	75.7(1)	O(10)–Cd(2) <sup>c</sup> –O(14) <sup>c</sup>	91.5(2)
O(3) <sup>b</sup> –Cd(1)–O(11)	168.1(2)	O(5)–Cd(2) <sup>c</sup> –O(13) <sup>c</sup>	94.1(1)	O(13) <sup>c</sup> –Cd(2) <sup>c</sup> –O(14) <sup>c</sup>	83.2(2)
O(3) <sup>b</sup> –Cd(1)–O(12)	85.2(1)	O(5)–Cd(2) <sup>c</sup> –O(14) <sup>c</sup>	85.5(2)		

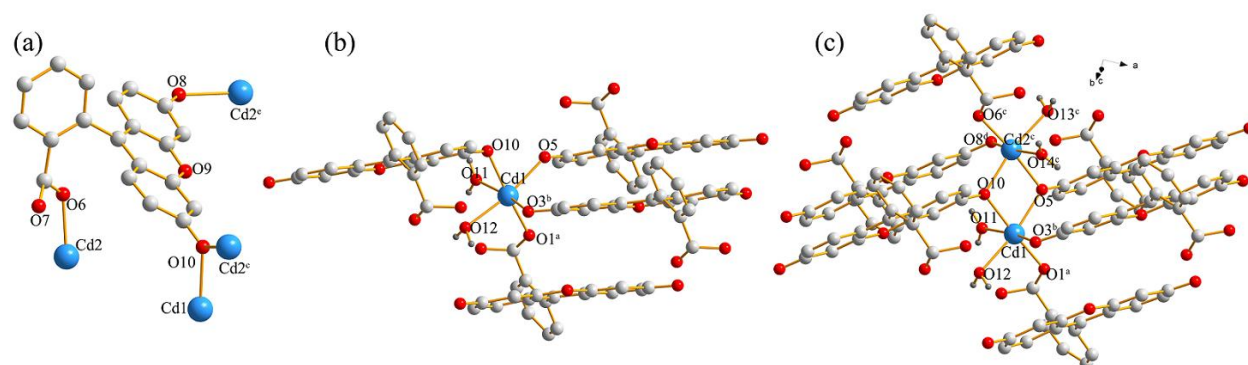
Symmetry transformation: a:  $x, y+1, z$ ; b:  $2-x, -y, 1-z$ ; c:  $x, -1+y, z$ ; d:  $1-x, 1-y, 1-z$

### 3 RESULTS AND DISCUSSION

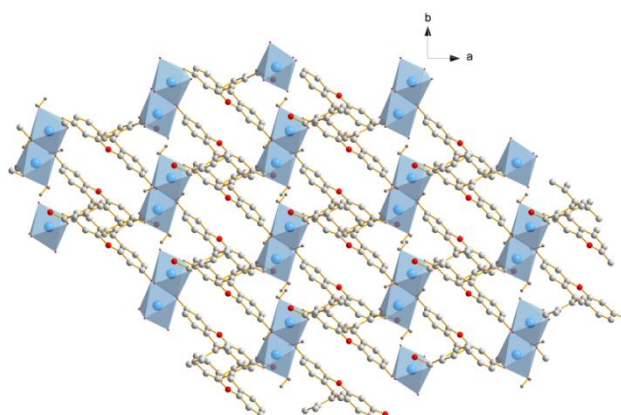
#### 3.1 Structural description

Single-crystal X-ray diffraction study reveals that **1** crystallizes in the monoclinic system with space group  $P2_1/n$ , showing a two-dimensional layer which packs up to afford the 3D structure. In one asymmetric unit, there exist two cadmium atoms, two fluorescein ligands, and four coordinating water molecules. There are four Cd atoms bonded with a single fluorescein ligand (Fig. 1a), while each Cd(II) ion is hexa-coordinated by four O from four different fluorescein ligands and two water molecules with octahedral coordination geometry (Fig. 1b). The disordered O atoms are simplified for clarification. In particular, the two adjacent Cd atoms are bonded up by two  $\mu$ -O from two independent fluorescein ligands (Fig. 1c), and each is connected with another two fluorescein ligands and two water molecules, forming a unique  $\text{Cd}_2\text{O}_{10}$  cluster. The Cd–O bond lengths vary from 2.218(4) to 2.361(5) Å while the Cd–O–Cd bond angles are  $104.076(1)^\circ$  and

104.388(1)°, and the O–Cd–O bond angles change from 75.711(1)° to 172.234(1)°. Two of the six coordinating fluorescein ligands related to this cluster contribute the two  $\mu$ -O atoms, O(5) and O(10); two give the other coordinating O atoms, O(3) and O(8); the rest two ligands provide the two coordinating O atoms on their carboxyl, O(1) and O(6); the other four coordinating sites are occupied by water molecules. Two kinds of weak  $\pi$ - $\pi$  interactions are found between two sets of parallel fluorescein ligands with the centroid-to-centroid distances as 4.312/4.317 Å and the perpendicular distances to be 3.326/3.387 Å, respectively. The  $\text{Cd}_2\text{O}_{10}$  clusters are linked up by fluorescein ligands *via* the weak  $\pi$ - $\pi$  interactions and the first seven kinds of hydrogen bond interactions (Table 2), affording the wonderful 2D layer structure (Fig. 2) which further packs up by weak  $\pi$ - $\pi$  interactions and the C(23)–H(23)  $\cdots$  O(14) hydrogen bond to form the whole 3D structure with two types of nano-channels (Fig. 3).



**Fig. 1.** Coordination environment of the Cd(II) ion compound 1. (a) Tetra-coordinated fluorescein. (b) Hexa-coordinated Cd ion. (c) Coordination environment of the  $\text{Cd}_2\text{O}_{10}$  cluster. Atoms: Cd, blue; O, red; C, grey; H, pale. Symmetry transformation: a:  $x, y+1, z$ ; b:  $2-x, -y, 1-z$ ; c:  $x, -1+y, z$ ; d:  $1-x, 1-y, 1-z$ ; e:  $1-x, 2-y, 1-z$



**Fig. 2.** 2D layer structure of compound 1 viewed from the  $c$ -axis

**Table 2.** Hydrogen Bond Lengths (Å) and Bond Angles (°)

D–H $\cdots$ A	d(D–H)	d(H $\cdots$ A)	d(H $\cdots$ A)	<(DHA)
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O(11)–H(11B) ··· O(16) <sup>a</sup>	0.89	1.80	2.518(2)	136
O(11)–H(11B) ··· O(20)	0.89	2.03	2.771(2)	140
O(12)–H(12A) ··· O(8) <sup>e</sup>	0.92	2.05	2.752(5)	132
O(13)–H(13B) ··· O(3) <sup>b</sup>	0.88	2.19	2.807(5)	127
O(14)–H(14B) ··· O(17)	0.91	2.00	5.653(1)	128
C(3)–H(3) ··· O(16)	0.93	2.39	2.741(2)	102
C(23)–H(23) ··· O(17)	0.93	2.38	2.726(2)	102
C(23)–H(23) ··· O(14) <sup>f</sup>	0.93	2.56	3.469(1)	167

Symmetry transformation: a:  $x, y+1, z$ ; b:  $2-x, -y, 1-z$ ; e:  $1-x, 2-y, 1-z$ ; f:  $3/2-x, y, 1/2-z$

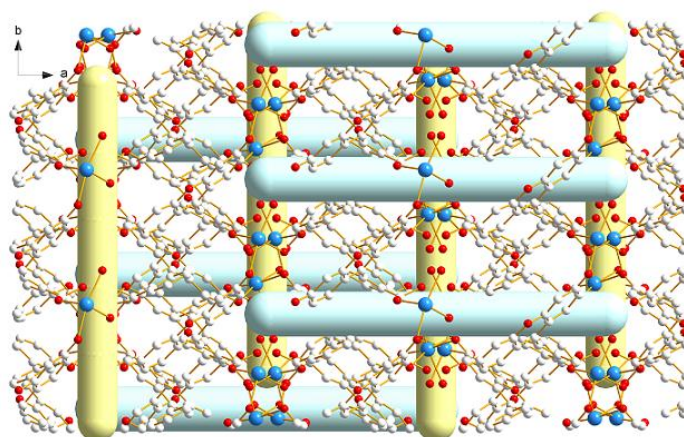


Fig. 3. 3D extended structure of **1** and side view of the two types of nano-channels in **1**

## 3.2 Characterizations

### 3.2.1 Powder X-ray diffraction

The crystalline phase purity of **1** was confirmed by powder X-ray diffraction. The experimental pattern agreed basically with that of simulation (Fig. 4a). The sample had been kept in open air for two days with no significant loss of crystallinity, indicating that **1** is quite stable towards water and oxygen.

### 3.2.2 IR spectroscopy

The infrared spectroscopy was performed to give the characteristic absorption of **1**. IR data (KBr,  $\text{cm}^{-1}$ ):  $\nu_s(\text{Ar-O}^-)$ : 1290 (s), 1328(s);  $\nu_s(\text{COO}^-)$ : 1513 (m), 1207 (m);  $\nu_{as}(\text{COO}^-)$ : 1577 (s), 1452 (s).

### 3.2.3 Thermo gravimetric analysis

Thermo gravimetric analysis was conducted to determine the contents of solvents and thermal stability of **1**. For **1**, the TGA curve (Fig. 4b) shows several processes of weight loss in the full range (30~900 °C) of measurement temperature. The first stage is 30~120 °C, corresponding to the loss of 10 water molecules of crystallization. The second one is 120~158 °C due to the release of four constitution water molecules. Then a platform from 158 to 475 °C follows, indicating the framework possesses quite excellent thermal stability in

this range of temperature. The sudden weight drop after 475 °C can be attributed to the collapse of the framework.

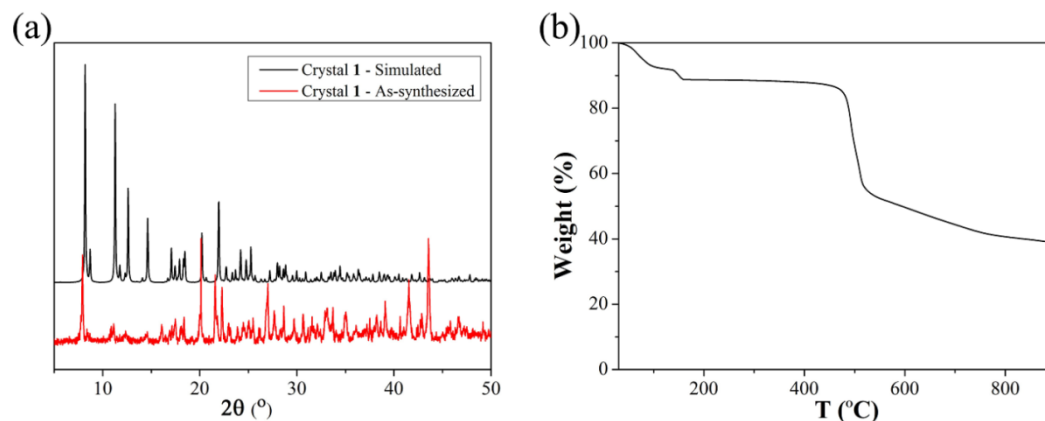


Fig. 4. (a) PXRD pattern of compound 1; (b) Thermo gravimetric analysis

## 4 CONCLUSION

In summary, a novel cadmium-fluorescein coordination complex has been synthesized *via* hydrothermal reaction and systematically characterized. Single-crystal X-ray diffraction analysis reveals that **1** possesses a unique  $\text{Cd}_2\text{O}_{10}$  core, which is linked up by fluorescein to afford a 2D layer that packs up to afford a 3D supramolecule, and two different types of 1D channels are found.

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ZHANG Guan-Hua(张冠华) WU Xiao-Yuan(吴小园)

WANG Sa-Sa(王洒洒) JIANG Xiao-Yu(蒋晓瑜) LU Can-Zhong(卢灿忠)

The synthesis and crystal structure of a fluorescein-based coordination complex are reported. This complex possesses a unique binuclear structure that two Cd atoms are bridged by two terminal oxygen atoms of two fluorescein ligands to afford the  $\text{Cd}_2\text{O}_{10}$  core, which is further linked up with each other to form the whole structure.

